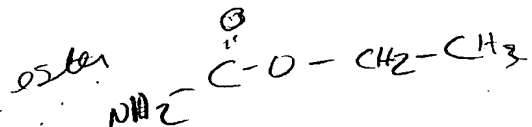
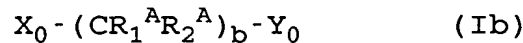


## CLAIMS



1. Fluorinated oligourethanes, having number average molecular weight lower than or equal to 9,000, the molecular weight determined by vapour pressure osmometry, said oligourethanes having a branched structure, optionally crosslinked, formed of the following monomers and macromers:

- a) aliphatic, cycloaliphatic or aromatic polyisocyanates, having NCO functionality, determined by titration with dibutylamine-HCl (ASTM D2572), higher than 2, preferably in the range 3-4;
- b) bifunctional hydrogenated monomers wherein the two functions are chemically different (heterofunctional monomers) having general formula:



wherein:

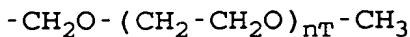
$R_1^A$  and  $R_2^A$ , equal to or different from each other, are H, aliphatic radicals from 1 to 10 carbon atoms, b is an integer in the range 1-20, preferably 1-10,

$X_0 = X_A H$  with  $X_A = O, S$ ,

$Y_0$  is anionic or cationic salifiable function, or,

when in the formula (Ib)  $X_0 = OH$ ,  $b = 1$ ,  $R_1^A = R_2^A =$

H,  $Y_0$  is an hydrophilic group preferably having formula



(Ib1)

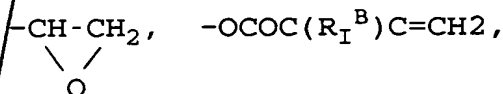
wherein nT is an integer in the range 3-20;

and one or more of the following compounds:

- c) bifunctional hydroxyl (per)fluoropolyethers (PFPE diols) having number average molecular weight in the range 400-3,000, preferably 700-2,000;
- e) monofunctional hydroxyl (per)fluoropolyethers ( $e^0$ ) or monofunctional hydroxyl (per)fluoroalkanes ( $e'$ ), having number average molecular weight in the range 300-1,000, preferably 400-800.

and optionally the following compounds:

- d) hydrogenated monomers capable to insert a crosslinkable chemical function in the oligourethane, having the formula (Ib), wherein  $R_1^A$ ,  $R_2^A$ , b and  $X_0$  are as above defined and  $Y_0$  is selected from the following functional groups:



wherein

$$R_T^B = H, CH_3/;$$

R<sub>x</sub> is a saturated C<sub>1</sub>-C<sub>5</sub>, preferably C<sub>1</sub>-C<sub>3</sub>, alkyl;

- d<sup>I</sup>) hydrogen-active compounds, capable to form bonds with the NCO functions stable at the hydrolysis but

lable to heat.

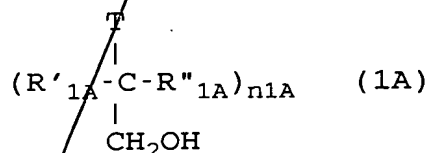
2. Oligourethanes according to claim 1 formed of a) + b) + c) and optionally e).

3. Oligourethanes according to ~~claims 1-2~~ <sup>claim 1</sup>, wherein the amounts of the components a) - c) are the following:

- component a): 10-70% by weight based on the total dry oligourethane, preferably 20-40% by weight;
- component b): the moles of b) are in a ratio with the moles of the NCO groups of a) ranging from  $1/3 : 1$  to  $2/3 : 1$ ;
- component c): the moles of the hydroxyl groups of component c) are in a ratio with the moles of the residual free NCO groups (the difference between the total ones and those reacted with b)) in the range 3-1.1, preferably 1.5-1.1; the component c) can also be absent and in this case component e) is present;
- when c) is absent, the amount by moles of the components e) + d) + d<sup>I</sup>) is in a ratio 1 : 1 with the moles of residual NCO (the difference between the initial total moles of a) and the moles of a) reacted with b)), and component e) must be present in an amount of at least 30% by weight based on the dry product;
- when component c) is present the total moles of the

components d) + d<sup>I</sup>) + e) are in a percentage in the range 0-90%, preferably 0-60% with respect to the moles of the component b).

4. Oligourethanes according to ~~claims 1-3~~ <sup>claim 1</sup>, wherein the monomers mentioned in b) have the function X<sub>A</sub>H with X<sub>A</sub> = O and the following structure formula:



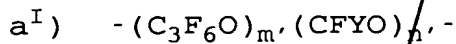
wherein T is SO<sub>3</sub>H, COOH, or a tertiary aminic group NR'<sub>N</sub>R''<sub>N</sub>, wherein R'<sub>N</sub> and R''<sub>N</sub>, equal to or different from each other, are a linear or branched C<sub>1</sub>-C<sub>6</sub> alkyl, R'<sub>1A</sub> and R''<sub>1A</sub>, equal to or different from each other, are hydrogen or a linear or branched C<sub>1</sub>-C<sub>4</sub> alkyl; n<sub>1A</sub> is an integer in the range 1-10, preferably between 1-4.

5. Oligourethanes according to claim 4 wherein, in formula (1A) T is a tertiary aminic group.

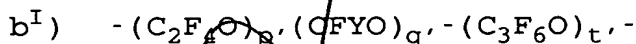
6. Oligourethanes according to ~~claims 1-5~~ <sup>claim 1</sup>, wherein the bifunctional (per)fluoropolyethers mentioned in c) have one or more of the following units statistically distributed along the chain: (C<sub>3</sub>F<sub>6</sub>O), (CFYO) wherein Y is F or CF<sub>3</sub>, (C<sub>2</sub>F<sub>4</sub>O), (CR<sub>4</sub>R<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>O) wherein R<sub>4</sub> and R<sub>5</sub> are equal to or different from each other and selected from H, Cl, and one fluorine atom of the

perfluoromethylene unit can be substituted with H, Cl or (per)fluoroalkyl, having from 1 to 4 carbon atoms.

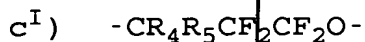
7. Oligourethanes according to claim 6, wherein the (per)fluoropolyethers are the following, with the perfluorooxyalkylene units statistically distributed along the chain:



wherein m' and n' are integers such as to give the above mentioned molecular weights, and m'/n' is in the range 5-40, n' being different from 0; Y is F or CF<sub>3</sub>; n' can also be 0;



wherein p' and q' are integers such that p'/q' ranges from 5 to 0.3, preferably from 2.7 to 0.5 and such that the molecular weight is within the above mentioned limits; t' is an integer with the meaning of m', Y = F or CF<sub>3</sub>; t' can be 0 and q'/(q'+p'+t') is equal to 1/10 or lower and the t'/p' ratio ranges from 0.2 to 6;



wherein R<sub>4</sub> and R<sub>5</sub> are equal to or different from each other and selected from H, Cl; the molecular weight such as to be within the above mentioned limits, and one fluorine atom of the

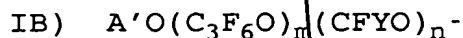
perfluoromethylene unit can be substituted with H, Cl or (per)fluoroalkyl, having for example from 1 to 4 carbon atoms;

the end groups of the bifunctional (per)fluoropoly-ethers c), equal to or different from each other, are of the  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{x_0}\text{CH}_2-$  type wherein  $x_0$  is an integer from 0 to 4, preferably from 0 to 2; in the preferred compounds  $x_0 = 0$ .

8. Oligourethanes according to ~~claims 1-7~~ <sup>claim 1</sup>, wherein the monomers d) have the formula (1A) wherein  $\text{R}'_{1A}$ ,  $\text{R}''_{1A}$  and  $n_{1A}$  are as above defined, T is selected from the groups which in component d) are at the place of the function  $\text{Y}_0$ , the OH group can optionally be substituted with a SH group.

9. Oligourethanes according to the previous ~~claims 1-8~~ <sup>claim 1</sup>, wherein the component e) is formed of hydroxyl mono-functional (per)fluoropolyethers, said (per)fluoropolyethers comprise one or more (per)fluorooxyalkylene units as indicated in claim 6.

10. Oligourethanes according to claim 9, wherein the (per)fluoropolyethers are the following, wherein the units are statistically distributed along the chain:



wherein Y is -F, -CF<sub>3</sub>; A' = -CF<sub>3</sub>, -C<sub>2</sub>F<sub>5</sub>, -C<sub>3</sub>F<sub>7</sub>,

-CF<sub>2</sub>Cl, C<sub>2</sub>F<sub>4</sub>Cl; the C<sub>3</sub>F<sub>6</sub>O and CFYO units are randomly distributed along the (per)fluoropolyether chain, m and n are integers, the m/n ratio is  $\geq 2$ ;

IIB) C<sub>3</sub>F<sub>7</sub>O(C<sub>3</sub>F<sub>6</sub>O)<sub>m</sub>-

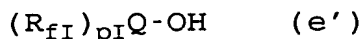
wherein m is an integer, wherein the number average molecular weight is that above mentioned;

IIIB) (C<sub>3</sub>F<sub>6</sub>O)<sub>m</sub>(C<sub>2</sub>F<sub>4</sub>O)<sub>n</sub>(CFYO)<sub>q</sub>

wherein Y is equal to -F, -CF<sub>3</sub>; m, n and q, different from zero, are integers such that the number average molecular weight is that indicated for the component e);

the end group being of the HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>x0</sub>CH<sub>2</sub>- type wherein x0 is an integer in the range 0-4, preferably 0-2, more preferably x0 = 0.

11. Oligourethanes according to ~~claims 1-8~~ <sup>claim 1</sup>, wherein the component e) is formed of hydroxyl monofunctional (per)fluoroalkanes having the formula:



wherein R<sub>fI</sub> is a fluoroalkyl C<sub>3</sub>-C<sub>30</sub>, preferably C<sub>3</sub>-C<sub>20</sub>, radical; pI is 1 or 2; Q is a bivalent aliphatic C<sub>1</sub>-C<sub>12</sub> or aromatic C<sub>6</sub>-C<sub>12</sub> linking bridge; ; Q can optionally contain heteroatoms such as N, O, S, or carbonylimino, sulphonylimino or carbonyl groups; Q can be unsubstituted or it is bound to substituents selected

from the following: halogen atoms, hydroxyl groups,  $C_1-C_6$  alkyl radicals; Q preferably does not contain double or triple bonds and is saturated; preferably Q is selected from the following divalent radicals:

$-CH_2-$ ,  $-C_2H_4-$ ,  $-SO_2N(R^5)C_2H_4-$ ,  $-SO_2N(R^5)CH_2CH(CH_3)-$ ,

$-C_2H_4SO_2N(R^5)C_4H_8-$ ,  $R^5$  is H or a  $C_1-C_4$  alkyl.

12. Oligourethanes according to <sup>claim 1</sup> ~~claims 1-11~~, wherein the number average molecular weight is in the range 2,000-9,000.

13. Compositions containing the oligourethanes according to <sup>claim 1</sup> ~~claims 1-12~~ in solution in organic solvent or in the form of aqueous dispersion.

14. A process for preparing the oligourethanes according to <sup>claim 1</sup> ~~claims 1-13~~ comprising the following steps when the component c) is present:

- 1) dissolution of the polyisocyanate component a), having average functionality NCO between 3 and 4, in an anhydrous dipolar aprotic organic solvent, so that the dry content in the organic solution is in the range 20-90% w/w;
- 2) addition of the bifunctional hydrogenated monomers indicated in b), optionally in admixture with the monomers mentioned in d) and/or the compounds indicated in d<sup>I</sup> and/or with the monohydroxyl



fluorinated macromers of type (e), in a total amount by moles such that the present hydroxyl groups by reacting with isocyanate lower the average NCO functionality of at least 1/3 with respect to the initial one, preferably such as to be in the range 2-2.5;

- 3) heating of the obtained mixture at a temperature between 50° and 80°C, in inert atmosphere, in the presence of tin organic compounds as catalysts, for the necessary time to reduce the NCO titre within the above mentioned limits (step 2), said titre determined by titration with dibutylamine-HCl (ASTM D2572);
- 4) addition drop by drop of the reaction mixture to a solution containing the hydroxyl bifunctional (per)fluoropolyethers c) in an anhydrous dipolar aprotic organic solvent, maintained at a temperature in the range 50°-80°C, the amount of said (per)fluoropolyethers being such that the OH/NCO molar ratio is between 2 and 1.1, and the organic solvent amount such that the resulting solution has a dry concentration in the range 30-60% w/w;
- 5) at the end of the reaction in 4), determined by IR spectroscopy from the disappearance of the band

corresponding to the NCO group, a solution of a base or of an acid is added to the mixture, depending on the type of the salifiable function present in the polymer, said base or acid dissolved in an organic preferably hydroxyl solvent, subsequently it is diluted with water under mechanical stirring, removing the organic solvents by evaporation at a reduced pressure.

15. A process according to ~~claims 1-13~~ <sup>claim 1</sup>, wherein in the second step (step 2) of the process of claim 14 component c) is not used but component e) in amounts by moles equal to that of the present NCO groups.
16. A process according to ~~claims 14-15~~ <sup>claim 14</sup>, wherein the hydroxyl organic solvent used in step 5) is an aliphatic alcohol having a low molecular weight, preferably C<sub>1</sub>-C<sub>3</sub>.
17. Use of the oligourethanes and of their compositions according to ~~claims 1-13~~ <sup>claim 1</sup> to form oil- hydro-repellent films.
18. Use according to claim 17, wherein films are obtained by crosslinking with polyisocyanates oligourethanes comprising the component c).
19. Use according to claim 17, wherein films are obtained by thermally or photochemically crosslinking oligourethanes comprising the optional component d).

20. Use according to claim 17, wherein films are obtained by thermally crosslinking oligourethanes comprising the components c) and d<sup>I</sup>).



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